Fabrication of Titania Nanostructures on Glass by Aluminum Anodizing and Sol-Gel Process

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Nanomaterials have exhibited a great potential for applications in various fields such as electronics, magnetism, optics, and energy storage or exchange, etc. So far, a variety of nanostructures (nanotubes, nanorods, nanofibers) have been synthesized by utilizing commercial porous alumina membrane as a template[1, 2], which is obtained by anodizing aluminum plate in acidic solutions under some conditions[3, 4]. The products of nanostructures, however, are usually in scattered state and difficult to apply to make practical devices. Titanium dioxide has been known as an effective photocatalysis. Much effort has been made to increase its surface area for higher photocatalytic activity. This study is aimed to create a novel nanotechnology in the fabrication of titanium dioxide nanostructures with large surface area on a glass substrate by combining techniques of aluminum anodizing and sol-gel process,[5] which is expected to apply in manufacturing practical devices or functional glass for photocatalysis and/or solar energy utilization, etc.

Highly pure aluminum film (99.99 %, ~ 2 μm), which is evaporated on a glass substrate with a conductive indium tin oxide (ITO) layer by a conventional RF-sputtering, was used as specimen. The specimen was first anodized potentiostaticly in a 10 % (vol.) phosphoric acid solution at 60 ~ 150 V and 4 ~ 10 °C, to obtain porous alumina structures with unit cell sizes in 110 ~ 450 nm. After removing the barrier layer and widening the pores of anodic alumina, the specimen was dip-coated in a TiO_2 solution and heated at 100 °C for 1 hr and at 400 °C for 2 hr, to get an Al_2O_3/TiO_2 composite nanostructure. The TiO_2 solution (~5 %) used in the sol-gel process was prepared by titanium isopropoxide, acetylacetone, distilled water and ethanol in a mole ratio of 1:1:3:20, and the viscosity of the solution was kept at about 2.4. Titania nanotubes array on glass was eventually fabricated after removing the anodic alumina by chemical etching in a solution containing 5 % H_3PO_4 and 2 % CrO_3. The morphology of the surface and the fracture cross-section of the specimens were observed by FESEM and TEM. The crystal structure of titania nanotubes was examined by XRD analysis. The UV-Vis transmittance spectra of the specimens were measured by a spectrophotometer. Moreover, in order to enhance the strength of titanium oxide nanotubes and the adhesion to the substrate, the fabrication of $TiO_2/SiO_2/TeO_2$ composite nanotubes was also investigated by the method above.

It was found that porous alumina structure with straight and paralleled pores was obtained by anodizing at potentials higher than 130 V, below which porous alumina with some branches was formed. The as-anodized specimens are transparent (95 ~ 100 T% in 550 nm), due to the thorough anodizing of aluminum sputtered on glass with a conductive ITO layer. The anodic alumina contains uniform pores with a thin and arched-shape barrier layer, which can be dissolved away along with the pore-widening, making possible the TiO_2 gel connect directly to the substrate in the sol-gel process. Figure 1 gives an example of TiO_2 nanotubes standing on a glass substrate obtained by successive Al anodizing (150 V) and sol-gel process. The TiO_2 nanotubes are about 200 nm in diameter with a wall in 40 nm-thick and 3 μm long. According to the pore density of anodic alumina and the dimensions of TiO_2 nanotubes, the surface areas of the TiO_2 nanotubes array in Fig.1 and the Al_2O_3/TiO_2 composite nanostructure (not shown) are calculated as about 450 and 200 times larger than that of flat film, respectively.

The crystal structure of titania nanostructures was identified through XRD analysis as anatase with preferential (101) facet, which is known to have higher photocatalytic activity. The crystal structure of titania was further confirmed by the diffraction pattern in TEM observation, and the size of titania crystals was evaluated as 5 ~ 20 nm. Figure 2 gives the UV-Vis transmittance spectra of various oxide nanostructures on a glass substrate. The TiO_2 nanostructures, both TiO_2 nanotubes array and Al_2O_3/TiO_2 composite layer, shows a strong absorbance within ultraviolet range, inferring a promising application in photocatalytic devices.

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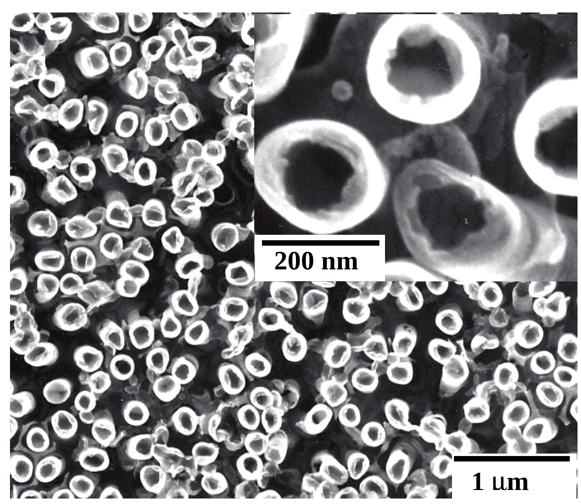

Fig.1 FESEM images (top view) of titania nanotubes array on glass substrate.

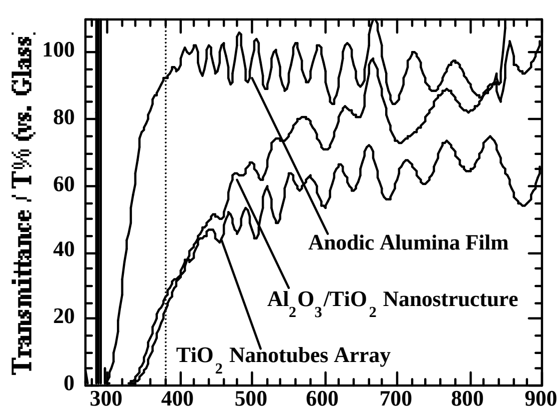

Fig. 2 UV-Vis Transmittance spectra of oxide nanostructures on glass substrate.